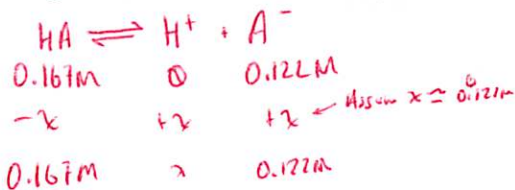


Buffer Problems (you will need to look up K_a values)

A buffer is prepared by adding 20.0 g of acetic acid and 20.0 g of sodium acetate to enough water to form 2.00 L of solution. Determine the pH of the buffer.

$$20.0 \text{ g HAc} \times \frac{1 \text{ mol HAc}}{60 \text{ g HAc}} \times \frac{1}{2.00 \text{ L}} = 0.167 \text{ M HAc}$$

$$20.0 \text{ g NaOAc} \times \frac{1 \text{ mol NaOAc}}{82.0 \text{ g NaOAc}} \times \frac{1}{2.00 \text{ L}} = 0.122 \text{ M NaOAc}$$



$$\frac{x(0.122 \text{ M})}{0.167 \text{ M}} = 1.8 \times 10^{-5} \quad [\text{H}^+] = x = 2.46 \times 10^{-5} \text{ M}$$

pH = 4.608

What is the ratio of HCO_3^- to H_2CO_3 in blood of pH 7.4? What is the ratio of HCO_3^- to H_2CO_3 in an exhausted marathon runner whose blood pH is 7.1?

$$\frac{K_a}{[\text{H}^+]} = \frac{[\text{A}^-]}{[\text{HA}]} = \frac{4.3 \times 10^{-7}}{3.9 \times 10^{-8}} = \frac{10.8}{1}$$

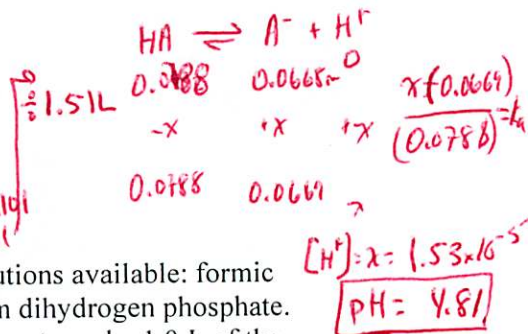
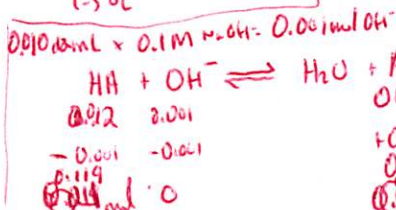
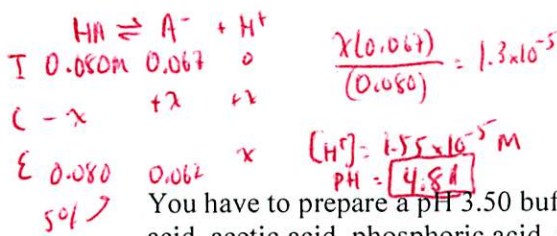
$K_a = 4.3 \times 10^{-7}$
 $[\text{H}^+] = 10^{-7.4} = 3.98 \times 10^{-8}$

$$[\text{H}^+] = 10^{-7.1} = 7.94 \times 10^{-8} \text{ M}$$

$$\frac{4.3 \times 10^{-7}}{7.94 \times 10^{-8}} = \frac{5.42}{1}$$

A buffer contains 0.12 mol of propionic acid and 0.10 mol of sodium propionate in 1.50 L. What is the pH of this buffer? What is the pH of this buffer after the addition of 10.0 mL of 0.10 M NaOH?

$$K_a = 1.3 \times 10^{-5} \quad [\text{HA}] = \frac{0.12 \text{ mol}}{1.50 \text{ L}} = 0.080 \text{ M} \quad [\text{A}^-] = \frac{0.10 \text{ mol}}{1.50 \text{ L}} = 0.067 \text{ M}$$



You have to prepare a pH 3.50 buffer, and you have the following 0.10 M solutions available: formic acid, acetic acid, phosphoric acid, sodium formate, sodium acetate, and sodium dihydrogen phosphate. Which solutions would you use? How many mL of each solution would you use to make 1.0 L of the buffer?

Formic $K_a = 1.8 \times 10^{-4}$

Acetic $K_a = 1.8 \times 10^{-5}$

Phosphoric $K_a = 7.5 \times 10^{-8}$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

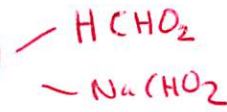
For optimal Buffer
 $\frac{[\text{A}^-]}{[\text{HA}]} = 1$ Thus, $\log \frac{[\text{A}^-]}{[\text{HA}]} = 0$

$3.50 = \text{p}K_a$

$\therefore \text{pH} = \text{p}K_a$

$K_a = 3.2 \times 10^{-4} \leftarrow \text{best}$

Use $\text{p}K_a$ next to that is for Formic Acid
 $\text{p}K_a = 3.74$



$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$3.50 = 3.74 + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\log \frac{[\text{A}^-]}{[\text{HA}]} = -0.24 \quad \frac{[\text{A}^-]}{[\text{HA}]} = \frac{0.57}{1}$$

$$\frac{1.8 \times 10^{-4}}{3.2 \times 10^{-4}} = \frac{[\text{A}^-]}{[\text{HA}]} = \frac{1 \text{ M}}{1.77 \text{ M}}$$

Assume $0.1 \text{ M} \times V_{\text{A}^-} + V_{\text{HA}} = 1.0 \text{ L}$
 $y = V_{\text{A}^-}$; $1 - y = V_{\text{HA}}$

$$0.57 = \frac{(0.1 \text{ M})(y) / 1 \text{ L}}{0.1 \text{ M}(1 - y) / 1 \text{ L}}$$

$$0.57(0.1 \text{ M}(1 - y)) = 0.1 y \rightarrow 0.057 - 0.057 y = 0.1 y$$

$y = 0.363 \text{ L}$
 $= 360 \text{ mL A}^-$
 640 mL HA

Titration Problems (Key Cont)

1. d. $20.1 \text{ mL} \times 0.200 \text{ M HCl} = 4.02 \text{ mmol HCl}$
 $4 \text{ mmol HCl} - 4.02 \text{ mmol KOH} = 0.020 \text{ mmol KOH}$
 $\frac{0.020 \text{ mmol KOH}}{40.1 \text{ mL}} = 4.98 \times 10^{-4} \text{ M OH}^-$
 $\text{pH} = 10.70$

e. $35.0 \text{ mL} \times 0.200 \text{ M KOH} = 7 \text{ mmol KOH}$
 $4 \text{ mmol} - 7 \text{ mmol} = 3.0 \text{ mmol KOH}$
 $\frac{3.0 \text{ mmol KOH}}{55.0 \text{ mL}} = 0.0545 \text{ M OH}^-$
 $\text{pH} = 12.74$

2. d. $35.0 \text{ mL} \times 0.150 \text{ M} = 5.25 \text{ mmol OH}^-$
 $\text{Oxalic acid } 0.150 \text{ M H}_2\text{A} \quad \frac{5.25 \text{ mmol OH}^-}{70 \text{ mL}} = 0.075 \text{ M}$
 $\text{H}_2\text{A} + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{HA}^-$
 $K_b = \frac{K_w}{1.8 \times 10^{-5}} = 5.55 \times 10^{-10} = \frac{x^2}{0.075 \text{ M}}$
 $[\text{OH}^-] = 6.45 \times 10^{-6} \text{ M} \quad \text{pH} = 8.81$

e. $35.5 \text{ mL} \times 0.150 \text{ M KOH} = 5.325 \text{ mmol KOH}$
 $5.325 \text{ mmol KOH} - 5.25 \text{ mmol HCl} = 0.075 \text{ mmol OH}^-$
 $\frac{0.075 \text{ mmol OH}^-}{70.5 \text{ mL}} = 1.06 \times 10^{-3} \text{ M OH}^-$
 $\text{pH} = 11.03$

f. $50.0 \text{ mL} \times 0.150 \text{ M KOH} = 7.50 \text{ mmol KOH}$
 $7.50 \text{ mmol KOH} - 5.25 \text{ mmol HCl} = 2.25 \text{ mmol OH}^-$
 $\frac{2.25 \text{ mmol OH}^-}{85 \text{ mL}} = 0.0265 \text{ M OH}^-$
 $\text{pH} = 12.42$

3. d. $35.0 \text{ mL} \times 0.025 \text{ M HCl} = 0.875 \text{ mmol HCl}$
 $0.90 \text{ mmol NH}_3 - 0.875 \text{ mmol HCl} = 2.5 \times 10^{-2} \text{ mmol NH}_3 \text{ left}$
 $\frac{2.5 \times 10^{-2} \text{ mmol NH}_3}{65 \text{ mL}} = 3.8 \times 10^{-4} \text{ M NH}_3$
 $\frac{0.875 \text{ mmol NH}_4^+}{65 \text{ mL}} = 1.34 \times 10^{-2} \text{ M NH}_4^+$
 $[\text{OH}^-] = \frac{(1.8 \times 10^{-5})(3.8 \times 10^{-4} \text{ M NH}_3)}{1.34 \times 10^{-2} \text{ M NH}_4^+} = 5.08 \times 10^{-7} \text{ M}$
 $\text{pH} = 7.71$

e. $36.0 \text{ mL} \times 0.025 \text{ M HCl} = 0.9 \text{ mmol HCl}$
 $0.9 \text{ mmol NH}_3 - 0.90 \text{ mmol HCl} = 0.00 \text{ mmol NH}_3$
 $\frac{0.90 \text{ mmol NH}_4^+}{66.0 \text{ mL}} = 1.36 \times 10^{-2} \text{ M NH}_4^+$
 $K_a = \frac{K_w}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$
 $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$

I	$1.36 \times 10^{-2} \text{ M}$	0	0
C	$-x$	$+x$	$+x$
E	1.36×10^{-2}	x	x

Assume x very small
 $\frac{x^2}{1.36 \times 10^{-2}} = 5.56 \times 10^{-10} \quad [\text{H}^+] = 8.69 \times 10^{-7} \text{ M}$
 $\text{pH} = 6.06$

3f $37.0 \text{ mL} \times 0.025 \text{ M HCl} = 0.925 \text{ mmol H}^+$
 $0.0725 \text{ mmol HCl} - 0.900 \text{ mmol HCl} = 0.025 \text{ mmol H}^+ \text{ left}$
 $\frac{0.025 \text{ mmol H}^+}{67 \text{ mL}} = 3.73 \times 10^{-4} \text{ M H}^+$
 $\text{pH} = 3.43$

4b Lactate $K_b = \frac{K_w}{1.38 \times 10^{-5}} = 7.25 \times 10^{-10}$

$\text{H}_2\text{O} + \text{A}^- \rightleftharpoons \text{HA} + \text{OH}^-$	
I 0.05M	0
C -x	+x
E 0.05M-x	x

$\frac{x^2}{0.05\text{M}} = 7.25 \times 10^{-10}$
 $[\text{OH}^-] = x = 6.02 \times 10^{-6} \text{ M}$
 $\text{pH} = 8.78$

Cresol purple
 Thymol Red
 phenolphthalein

4c $\text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{H}^+$

$\text{H}_2\text{O} \text{ CO}_3^{2-} \rightarrow \text{HCO}_3^- + \text{OH}^-$	
I 0.05M	0
C -x	+x
E 0.05M-x	x

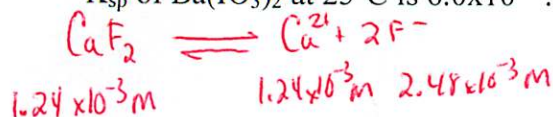
$K_b = \frac{K_w}{6.1 \times 10^{-5}} = 1.64 \times 10^{-10}$
 $\frac{x^2}{0.05\text{M}} = 1.64 \times 10^{-10}$
 $[\text{OH}^-] = x = 2.86 \times 10^{-6}$
 $\text{pH} = 8.46$

Cresol purple
 Thymol Red
 phenolphthalein

9.1

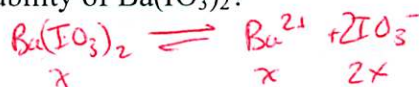
K_{sp} Problems

1. The molar solubility of CaF₂ at 35°C is $1.24 \times 10^{-3} \text{ mol L}^{-1}$, what is the K_{sp} at this temperature? The K_{sp} of Ba(IO₃)₂ at 25°C is 6.0×10^{-10} . What is the molar solubility of Ba(IO₃)₂?



$$K_{sp} = (1.24 \times 10^{-3})^2 (2.48 \times 10^{-3})^2 = 7.63 \times 10^{-9}$$

$[\text{Ca}^{2+}] [\text{F}^-]^2$

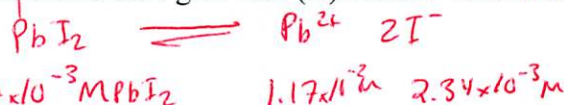


$$K_{sp} = x(2x)^2 = 4x^3 = 6.0 \times 10^{-10} \quad x = 5.31 \times 10^{-4} \text{ M}$$

2. A saturated 1.00 L lead (II) iodide solution at 25°C contains 0.54 g of lead (II) iodide. Calculate the solubility product constant.

$$0.54 \text{ g PbI}_2 \times \frac{1 \text{ mol PbI}_2}{461 \text{ g PbI}_2} = 0.00117 \text{ mol PbI}_2$$

1.00 L



$$K_{sp} = [\text{Pb}^{2+}][\text{I}^-]^2 = (1.17 \times 10^{-3})(2.34 \times 10^{-3})^2 = 6.43 \times 10^{-9}$$

3. Calculate the solubility of Mn(OH)₂ in grams per liter when buffered at pH 7.0, 9.5, and 11.8.

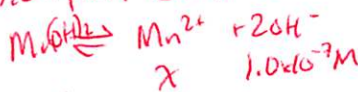
$$K_{sp} \text{ Mn(OH)}_2 = 2 \times 10^{-13}$$

$$\text{pH} = 7.0 = \text{pOH} + \log[\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$$

$$\text{pH} = 7.0 \quad K_{sp} = [\text{Mn}^{2+}][\text{OH}^-]^2 = 2 \times 10^{-13}$$

$4x^3 = 2 \times 10^{-13}$

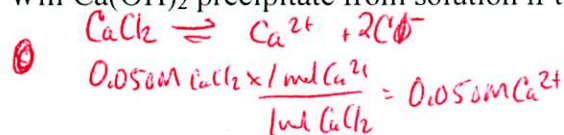
$[\text{Mn}^{2+}] = 3.6 \times 10^{-5} \text{ M}$



$$2 \times 10^{-13} = (x)(1.0 \times 10^{-7})^2$$

$$[\text{Mn}^{2+}] = [\text{Mn(OH)}_2] = x = 20 \text{ M Mn(OH)}_2 \times \frac{88.94 \text{ g}}{1 \text{ L}} = 1.78 \times 10^3 \text{ g/L}$$

4. Will Ca(OH)₂ precipitate from solution if the pH of a 0.050 M solution of CaCl₂ is adjusted to 8.0?



$$\text{pH} 8.0 \rightarrow [\text{OH}^-] = 1 \times 10^{-6} \text{ M}$$

$$Q = [\text{Ca}^{2+}][\text{OH}^-]^2 = (0.050 \text{ M})(1 \times 10^{-6} \text{ M})^2 = 5 \times 10^{-14} < K_{sp}$$

No Hydrolysis is Ca²⁺/Cl⁻ doesn't react in base

No

5. Will AgIO₃ precipitate when 100. mL of 0.010 M AgNO₃ is mixed with 10. mL of 0.015 M NaIO₃? (K_{sp} of AgIO₃ is 3.1×10^{-8})

$$100. \text{ mL} \times 0.010 \text{ M AgNO}_3 = 1 \text{ mmol Ag}^+ \times \frac{1}{110 \text{ mL}} = 9.09 \times 10^{-3} \text{ M Ag}^+$$

$$10. \text{ mL} \times 0.015 \text{ M NaIO}_3 = 0.15 \text{ mmol IO}_3^- \times \frac{1}{110 \text{ mL}} = 1.36 \times 10^{-3} \text{ M IO}_3^-$$

$$Q = (9.09 \times 10^{-3})(1.36 \times 10^{-3}) = 1.24 \times 10^{-5} > 3.1 \times 10^{-8}$$

Yes

$$Q > K_{sp}$$

6. A solution of Na₂SO₄ is added dropwise to a solution that is 0.010 M in Ba²⁺ and 0.010 M in Sr²⁺. What concentration of SO₄²⁻ is necessary to begin precipitation? Which cation precipitates first?

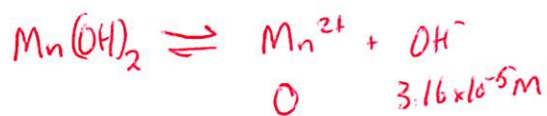
↳ Ba²⁺ b/c lower K_{sp} value

$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

$$(0.010 \text{ M})(x) = 1.59 \times 10^{-9}$$

$$x = 1.59 \times 10^{-7} \text{ M SO}_4^{2-}$$

Q3 @ pH 9.5 = $[OH^-] = 3.16 \times 10^{-5} M$



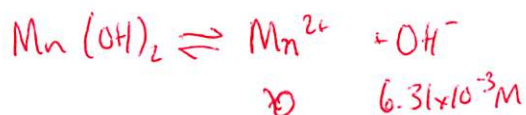
Assume x very small

$$2 \times 10^{-13} = x (3.16 \times 10^{-5})^2$$

$$[Mn^{2+}] = [Mn(OH)_2] = x = 2.00 \times 10^{-4} M$$

$$2.00 \times 10^{-4} M Mn(OH)_2 \times \frac{88.94 g Mn(OH)_2}{1 mol} = \boxed{\frac{1.77 \times 10^{-2} g Mn(OH)_2}{L}}$$

Q3 pH 11.8 $[OH^-] = 6.31 \times 10^{-3} M OH^-$



$$2 \times 10^{-13} = x (6.31 \times 10^{-3})^2$$

$$[Mn^{2+}] = [Mn(OH)_2] = x = 5.02 \times 10^{-9} M \times \frac{88.94 g}{L}$$

$$\boxed{\frac{4.47 \times 10^{-7} g}{L}}$$



I 0.10M

0

0

C - x

+x

+x

E 0.10M

~~0.10M~~

1.34×10^{-3}

1.34×10^{-4}

$$pH = pK_a + \log \left(\frac{A^-}{HA} \right)$$

$$4.3 = 4.74 + \log \left(\frac{0.10M}{20. + x} \right)$$

$$\left(\frac{0.10M}{20. + x} \right)$$

$$1.8 \times 10^{-5} = \frac{x^2}{0.10M}$$

$$K_a = \text{(correct)}$$

$$1.34 \times 10^{-3}$$

H

0.14

0.3

0.47

0.16

0.17

$$\frac{(0.14)(0.098)}{1.0mL}$$

0.015